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Discussions on Session 3A: Quantum dynamic theory

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Auditor: A. Ishizaki (University of California, Berkeley

A. Nitzan: Before opening the discussion, I want to express my puzzlement after these two talks since Shaul Mukamel insisted that inherent entanglement is a nonlinear issue while Birgitta Whaley described entanglement in a linear space. To put it differently, Shaul showed me that quantum computing is intrinsically nonlinear and Ronnie Kosloff showed me that I can build a quantum computer from a system of linearly coupled harmonic oscillators. And so I would hope that during the discussion maybe I will learn a little bit about this question.

V. Vedral: I just want to make one comment to maybe clarify this issue because it may not have been stated clearly in the talks. You have probably three places where entanglement could matter. One is in the system itself, and I think this is the talk we just heard by Birgitta. And it may or may not play any role in terms of speed up and we saw this very beautiful illustration that actually in FMO, probably, there is no advantage.

A. Nitzan: When you said in the system itself did you mean in the linear system itself?

V. Vedral: Meaning in the molecular complex itself. We have a good definition of what it means to be entangled, and I think your second slide actually shows what it means to have entanglement. I think what Shaul was talking about was probing the system. And I think there we also have developed very nice techniques of interferometry, where we know that we can beat the shot noise limit if we use highly entangled states. But this is now entanglement in the field that probes the system. And, of course, you also have coupling between the two, and you will also get entanglement between two. But it is very important to keep these things separate. So I think this talk was mainly about entanglement in the system, whereas the first one was about probing with entangled states.

S. Mukamel: Yes, this is a correct point. But, my main point is not that. Regardless of how we probe it, my point is that if I have just classical normal modes and I have the system that is harmonic, I can think of it in term of non-entangled normal modes or in terms of entangled local particles. Both are legitimate and it is a matter of choice whether you want to use one description or another. But you have the option to avoid using the notion of entanglement by using normal modes but doing that will pop up in the nonlinearities. Birgitta was using the notion of entanglement for the linear response in order to gain insight and to look at the system in another way. So, it's just optional.

B. Whaley: Yes.

V. Vedral: Let me try to comment on that as well. You can get rid of entanglement if you make a global transformation. But, if you clearly first start by defining what your subsystems are, namely here I have one spatial

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region and here I have another one, then you cannot get rid of entanglement by locally transforming. So when you make a mode transformation it will invariably move from space into momentum, if you like, k-space. So I think, in that sense, you could get rid of entanglement. But, now you are talking about completely different subsystems. So, you cannot get rid of entanglement if you properly define your subsystem initially.

A. Nitzan: On this subject?

T. Renger: I have a question about this steady state entanglement that Birgitta was talking about. Is it just a kind of entanglement that Shaul would call normal mode entanglement? Or is it deviation from that?

B. Whaley: Shaul would say this doesn't exist.

T. Renger: So, it's just that the exciton states are delocalized, and you relax into delocalized states and you have coherence between sites.

B. Whaley: It's equivalent to that.

T. Renger: Or is there some deviation from that?

B. Whaley: No, mathematically it's equivalent.

V. Vedral: Let me try to make another comment just on this point, if I may.

A. Nitzan: Let us give some other people a chance.

V. Vedral: It is relevant for this, but ...

A. Nitzan: We will come back.

G. Engel: In trying to sort this issue out, I notice a couple of things. One is that the entanglement measure that you used, Birgitta, is basis-set dependent. Is the site-basis why we see this? Shaul, if we looked at the excitonic basis, we would not. So, entanglement to some degree is a measure of our surprise. If the site basis is a natural basis, as one might expect when you separate these particles to infinite distance then suddenly this measure is important. As you say, for the hydrogen molecule, if the electrons are too close we cannot measure them individually, it's not. But, in particular, in the FMO complex, the chlorosome and the reaction center, you expressed the coupling to those two external elements, that probably projects quite naturally onto the site-basis. And in that regard the site-basis is somewhat of a natural basis for this complex, even though for spectroscopic measurements, where we get energy out, it tends to be more natural in the excitonic basis. So, in some sense, it seems that this measure of entanglement is a degree of surprise, and it measures in some sense, how well we are thinking about problem. It seems like an intellectual construct for how to think about the system, if we should think in site-basis or we should think in excitonic basis.

B. Whaley: Right. Mode entanglement is always dependent on the basis you choose. It is always a question, which modes do you want to use? Are there other reasons to use those modes? Or are they the most naturally or physically relevant modes? I would argue that the site-basis is a suitable choice for the spatially separated objects. And again to be looking at larger and larger systems the spatial separation is important and that makes the site-basis a natural and attractive basis.

G. Engel: And I think there are two reasons that it is attractive and it is important to sort between them. One is that it is pleasing when we see a crystal structure to choose individual chromophores. I would argue that it is not a particularly good reason to use the site-basis. However, if the trap, the reaction center couples in the site-basis that would make this much more relevant. But, I think we have to be careful. It is also attractive in the hydrogen molecule to pick out individual atoms and that's obviously not such a good selection.

B. Whaley: You cannot actually distinguish the electrons in the hydrogen molecule because they are occupying the same spatial region. Here, your excitations are occupying different spatial regions.

G. Engel: It is not quite as clear in a coupled system that that is necessarily true when you have off-diagonal elements of the Hamiltonian.

R. Harris: You have to avoid describing these electrons because like Shell's analogy if you do non-interacting electrons in physical space, it is Slater determinant. If you do it in second-quantized space, it is a product of the operators.

B. Whaley: All I wanted to say was that the notion of entanglement in quantum information refers to distinguishable objects which can be addressed individually. So whatever you are doing in molecular systems unless you can address electrons individually you better not talk about entanglement.

A. Buchleitner: So, firstly, a very brief remark back to Bob. We have to be careful in the formal definition, also Vlatko and Martin said something about that. Concerning the measurement of entanglement of indistinguishable particles, that is a different problem, and we should screen that out, for the moment to clarify the discussion.
And secondly, the question is, why does the kind of entanglement described by Birgitta is present here? Really it is present due to certain mathematical definitions. But I think at the end we should insist on a question which was asked at the beginning. We should insist on physical phenomena that we can predict due to entanglement being present in the system and not for which we need entanglement as a concept as compared, or in contrast, or beyond multi-particle multi-site coherence. Therefore I guess that Vlatko or Martin can comment on that. We should look for measurements which correlate measurement results on different sites in the complex, for example, and then we can come up with some kind of witness or however you would call it a Bell's inequality, which then falsifies the predictions of classical probability theory on these correlations. Okay, then we are done.

R. Cogdell: My confusion in this is that I have a rather poor understanding, but I can understand a Bell's inequality. In this system, none of these sites, different chlorophylls, you can see them in the structure, they are independent. But photo-chemically, they are not independent. In the collective of the whole, some of those are more strongly linked to each other. So, they can be effectively grouped into units that you can address as a unit. But actually even then it's never zero of any of them. So I don't that you can make the measurements, which would allow you to say there is the Bell's inequality, and therefore, I don't understand the term of entanglement in this system.

A. Buchleitner: If I may directly reply to that. That's a question which I have to this community of biochemists: whether you can do such experiments. That's one of the important questions we have to ask. One of the issues that is here is that, we don't have so much knowledge about manifestations of entanglement in the dynamics. I think that is a very interesting subject. And I think that is what we have to deal with.

A. Nitzan: We will continue that, I would hope before we take coffee, also, maybe somebody could address the issue whether biologically speaking entanglement is dead or alive. But let's continue with this. Please.

V. Vedral: You know, I will probably cover lots of these in my talk. I don't have to speak now about it. But, I think we in fact have some evidence on the contrary. That entanglement and even other forms of correlations are not necessarily connected with the speedup. If your goal is to optimize the transfer and the probability of getting from A to B, then maybe it's not really connected with that at all. Very unclear, very unclear.

M. Plenio: I'd like to also comment on that. One may not even expect that these entanglement measures or quantifiers that have been defined in quantum information under very very specific experimental setting, namely that you have distant labs and spatial separation actually really would tell you something straightforward about the efficiency of energy transport because it is really a different problem here that you have, as Richard Cogdell said, you don't have natural spatial separation, you can choose different bases, you have dynamics, directly interacting particles. It is not at all clear that the concept we have introduced in quantum information under the specific spatial separation aspect, would actually even give us insight here. This is a point that we have to think a little bit more carefully which of these concepts we can transfer to quantum effects in biology, and learn something from them. Or

whether we actually have to define new concepts that are more well adapted to the specific situation here.

A. Nitzan: Any of our speakers want to comment on this?

S. Mukamel: Yes, I want to just summarize in responding to this question. Basically, the difference between our viewpoints is that, as far as linear response is concerned, you have the option. It's a question of taste or whatever you feel natural. In one language you say there is exciton delocalization, in the other language you say that there is entanglement. It is completely equivalent. But, once you go to the nonlinear response you don't have this option. Because even if you got rid of the entanglement in the linear response, you have no control over the manybody states, and this is where the genuine entanglement will enter. And the other point is in terms of terminology. When we say "entangled state", it means that this is a property of the state. Actually it is not so. It is a property also of the degrees of freedom that we choose to describe the state. So, entanglement is not an objective property of the state. But, it also has to do with how we choose to describe it.

A. Nitzan: Does it mean that it depends on the probe as well as on the system?

S. Mukamel: No no, regardless of the probe. Just from the mathematical viewpoint. If I describe it with one set of degrees of freedom or another set of degrees of freedom. Now whether this can be accessed experimentally is a separate issue.

G. Engel: The nonlinear entanglement should therefore show up in the dynamics of the system. Is that reasonable? You cannot get away from it. You should be able to see this in the Hamiltonian basis and the elements of the system.

S. Mukamel: Once you go to higher excitations.

G. Engel: Yes.

Y. Tanimura: Here you show the result of entanglement. But, that's depending on how the heat bath is coupled. Right?

B. Whaley: How?

Y. Tanimura: Heat bath, environment.

B. Whaley: Yes.

Y. Tanimura: So, if the law of the coupling changes, the results may be changed.

B. Whaley: I showed you results from Redfield's calculations.

Y. Tanimura: What I mean is suppose if each two-level system couples to the heat bath differently.

B. Whaley: Sure. Of course there will be because it is a dynamical quantity and it will depend on the details of dynamics.

Y. Tanimura: Yes, certainly. So then, this is my real question. This is probably for Graham. Can you actually measure the entanglement by means of laser spectroscopy?

B. Whaley: Well, we are working on that. If you can do process tomography, you can do that, too. What is important here, is the full density matrix, and the third order nonlinear spectroscopy.

Y. Tanimura: I developed the reduced hierarchy equation approach to calculate the nonlinear response. I think the nonlinear response probably can show that. But, I don't know how it can be related to the entanglement and spectroscopy.

A. Olaya-Castro: Could you please go back to your slide in which the hierarchichal equation was compared with Redfield and Lindblad. When you were talking about these results, you mentioned that these show robustness of the kind of entanglement that you have in the system. Is that correct? So when you were describing this slide you mentioned that the comparisons that you are making confirm that the results that you are obtaining are "robust".

B. Whaley: I mean here the "robustness" with respect to the details of the models. Provided most importantly though, that you cannot run these models at infinite temperature. Then you wouldn't get anything. So, the temperature has to be in some way described correctly.

A. Olaya-Castro: Yes. So I am a little bit confused about what you mean by "robustness". Because as far as I can see your results are comparing the hierarchy equation with the Lindblad, and the secular approximation. What this is saying is that the parameters that you are using, confirm that a description within the Lindblad form is not so bad for this system given the fact that you have the two curves nearly overlapping. Of course, at short times they are going to differ. We know very well the Markov approximation does not work at short times. But, at long times it seems that the dynamics of your system are as well described with a weak coupling approximation as with the hierarchy equation.

B. Whaley: I wouldn't say the dynamics of the system, not the entire dynamics of the system. All I am saying is that the global entanglement is not exactly what I mean by robustness.

A. Olaya-Castro: So, I would say then that the dynamics of coherences of your system are quantified by the off-diagonal element.

B. Whaley: This is global entanglement. It's integrating over all of coherences in some way.

A. Olaya-Castro: So then, I need to ask a question here. If you did the same kind of calculations, I mean, comparisons now just by the off-diagonal elements these bi-partitions that you do computing with the concurrence, will these lines overlap as well?

B. Whaley: Maybe Aki can answer this point? If you compare the concurrence with the Lindblad?

A. Olaya-Castro: My point here is the following: It is very clear that you don't need a very sophisticated numerical description to be able to capture the early time-evolution of the coherences in the system from the calculations. But, it is also clear that at long times the description given by a weak-coupling coupling approximation is not so bad.

B. Whaley: It is not so bad for this particular quantity.

A. Olaya-Castro: Which is the quantity that essentially quantifies the quantum nature of the transfer.

B. Whaley: I cannot guarantee you that it is equally good for the individual concurrences.

A. Olaya-Castro: I totally agree. It's just that this quantity that you are using is essentially quantifying the deviation of your dynamic process from a completely classical one. This quantity is essentially quantifying the quantum nature of your transfer. As far as that is concerned, it doesn't seem too bad.

B. Whaley: No no, that's why I'm showing it to you.

A. Olaya-Castro: No no. I just want to point out that, because I think it is an interesting point. So, we don't require a very sophisticated theory to capture the details of short time dynamics, etc. But it seems that theories such as Lindblad, or weak coupling approximation, are not too bad.

B. Whaley: The most important thing, we found, is to have a good representation of the temperature.

A. Nitzan: But I want to come back to this issue whether this entanglement concept is useful in biology, maybe I will ask the speakers in the following way: when we think of transport, we can think of transport of metal particles, energy, or information, and I think it's established and we all agree that entanglement is very important in transporting information. Is it really important in transporting energy or particles?

S. Mukamel: The way that I look at it, entanglement is synonyms to having delocalized states. This issue has been discussed for ages in the molecular crystal literature. Mike Fayer was looking for it long ago in low-temperature crystals. And the idea is that if you have delocalization, transport can be faster and it could be more efficient, of course. To what extent it is crucial for the quantum yield in biology, I think all the evidence done by several groups say that it is something like a 5 to 10 percent effect. So it's there, but it's not decisive, as far as I can tell.

B. Whaley: I agree. I would say one more thing, which is all of the theoretical studies to date have been done on this very small system, FMO and maybe Aki's calculation for LHCII. But there are much larger systems out there, which open up completely different possibilities. For instance, a Chlorosome, this huge thing on top of FMO. This has a helical structure and has extensive exciton delocalization. Then the question comes, can a natural system possibly have multiple exctions. I think it's an open question as to what would happen there and what role it plays.

Y.-C. Cheng: So, I guess that delocalization is a good word that in the chemistry or physics community. Now, all the entanglement that you quantify or you measure here is basically the delocalization in the site basis. Your eigenstate naturally a delocalized exciton state and we know that in photosynthetic system the idea of photosynthetic exciton is very important. So, I'm a little bit confused about this idea of entanglement actually brings anything new in addition to use of delocalization to describe everything here?

B. Whaley: It is a very good point. It is not clear. I don't think it is clear whether there is a biologically role and whether there is anything more that we have learned here beyond the coherences. It is certainly true that we know that mode entanglement can be used from quantum information. Whether or not biology is doing anything like this is a really a very hard question to answer.

G.D. Scholes: I add something to Yuan-Chung. It is true that in photosynthesis we are often been interested in how excitation is collectively shared among molecules like in LH2. We like to talk about the participation ratio that is the measure of how many molecules collectively share the excitation. What entanglement brings to this point of view is something additional is how molecules share excitation under decoherence, and it gives a better resolution picture of how the excitation is shared. For example, you can show density matrices for systems like this that have identical participation ratio, but quite different entanglement measures. It's because entanglement measures, the various measures can tell you how the excitation is distributed, not just how many molecules are sharing the excitation. So, I think, in my point of view, this is something it brings additional to the discussion.

B. Whaley: It is a good point.

S. Mukamel: A comment on that. If I look at the density matrix of the exciton, you can define a length associated with the diagonal elements and a length associated with the off-diagonal elements. These are two different measures which I can also define using delocalization. Again, I don't need to use the term entanglement. We have used this fifteen years ago, to calculate superradiance in aggregates. To calculate the way they go for it in order to emit. We found that this off-diagonal length is directly associated with superradiance. So again, this is another measure of localization.

J. Klinman: I have a question about the protein. There is so much focus on chromophores. First of all, there are proteins which are presumably controlling this phenomenon. So, you have crystal structures of FMO, the light harvesting complex, you have sequences. If you do sequence alignments, are there regions that are conserved? Are there regions that are variable? Are there co-compensation? So you have one residue that changes, then there is a compensatory change on an interacting residue. Looking at the environment and how rigid is environment? And how essential is that rigidity to get this coherence. All these questions that need to go beyond just looking at the chromophores. I don't know what your answers are. But, I'm asking the question.

B. Whaley: I agree 100%. And that is actually the task in the next few years to figure out what the proteins are really doing in detail. Maybe Richard could say more about that.

R. Cogdell: You can look at that sort of thing in LH2 by doing single molecule spectroscopy at low temperatures and looking at the way in which fluctuations in the protein structure affect the spectroscopic readout from the single molecules. What we have not done is to actually then take site directed mutants of the protein and really try to localize which areas of the protein are causing that spectroscopic readout changes of the pigments using the pigments to report changes in the protein and then fill that into some of these 2D spectroscopy that you can do.

J. Klinman: Maybe you will get a different exit channel even through your mutagenesis.

R. Cogdell: Absolutely. This is certainly something we should be doing in the future. This is well tractable. My comment was, Shaul was saying if entanglement is important it could only have a 5 or 10 percent effect. If you take an evolutionary point of view, 5 or 10 percent is a tremendous effect. If you are trying to build up in competition one organism versus another, 5% advantage, I mean, one bacterium will outgrow the other one within a few days. Evolutionarily speaking, if that is an advantage, a 5% effect is an enormous effect. Evolution deals with a fraction of a percent over many many years of competition.

A. Nitzan: But, by this argument all of us should have been quantum objects. Right?

R. Cogdell: No no, that's a complete mistake. That's assuming it's important. What I was saying is if that is an important effect, that is a large effect on the evolutional timescale. So, you can dismiss it and say it is only a 5 or 10 percent effect but on the evolutionary timescale, that is an enormous advantage if it is true. The question I have: is it true?

A. Nitzan: Last question or comment.

R. Kosloff: This is a comment rather than a question. Because I think on one hand there is entanglement and then there is correlation. What we mean by entanglement really is that we want to see extra quantum correlation beyond classical correlation. This is what we are looking at. We are asking is there extra quantum correlations in biological systems. I think Birgitta said something important, it is very temperature dependent. You can show, if you have something and you take a normal mode structure and it is entangled in a local structure. You raise the temperature the entanglement disappears. It is what is called the death of entanglement. If you take a high-temperature system, you can't see quantum correlations. If you go to 77K you can sometimes see quantum correlations. At 300K they just won't be there. That's a comment.

B. Whaley: This is 300K... No, actually there is not a very strong temperature dependence on the long time behavior.